CD221. LECTURE 6. THE FUNDAMENTAL EQUATION OF THE EINSTEIN SOLID

• <u>Deriving the fundamental equation of the Einstein solid</u>

As the examples of the Einstein solid have illustrated, the multiplicity Ω is a function both of the solid's bulk energy U and of the number of particles N that it's made up of. Had we been able to devise an even more realistic model of the solid, we would have found that Ω is also a function of its size V. In general, then, $\Omega = \Omega(U,V,N)$, which means that the entropy as calculated from the Boltzmann equation,

$$S = k_B \ln \Omega \tag{1}$$

is likewise a function of U, V and N, in general. What the calculation of Ω therefore leads to is a fundamental relation, viz., $S = S(U,V,N)$, and this, of course, provides complete knowledge of the thermodynamic properties of the system.

For the Einstein solid, we have found that the multiplicity is given by

$$\Omega(U,N) = \frac{(U + N - 1)!}{U! \times (N - 1)!} \tag{2}$$

What is the structure of the fundamental relation that is obtained from this relation?

To get S from Ω, one simply plugs Eq. (2) into Eq. (1), but a few minor changes to Eq. (2) need to be made first. In a real solid, each of the atoms can vibrate harmonically along *three* independent directions. So a solid of N oscillators is actually made up of $N/3$ atoms. To model a solid of N atoms, therefore, the solid really needs to be made up of $3N$ oscillators. So replacing N in Eq. (2) by $3N$, and re-introducing factor of $\hbar\omega$ in the terms involving U, our amended expression for Ω now reads

$$\Omega(U,N) = \frac{(U/\hbar\omega + 3N - 1)!}{(U/\hbar\omega)! \times (3N - 1)!} \tag{3}$$

which can be simplified somewhat by noting that both U and N are very large, so the factors of unity can be omitted. This leaves us with

$$\Omega(U,N) = \frac{(U/\hbar\omega + 3N)!}{(U/\hbar\omega)! \times (3N)!} \tag{4}$$

Taking logs, Eq. (4) becomes

$$\ln \Omega = \ln(U/\hbar\omega + 3N)! - \ln(U/\hbar\omega)! - \ln(3N)! \tag{5}$$

Further simplification of this expression is possible by introducing a mathematical result known as Stirling's approximation, which we'll now derive.

• Stirling's Approximation

The starting point of this approximation is the following identity for factorials:

$$n! = \int_0^\infty dx\, x^n e^{-x} \tag{6}$$

(which can be verified by integrating the RHS by parts.) The integrand of Eq. (6), which we'll denote $f(x)$, is the product of a rapidly increasing function, x^n, and a rapidly decreasing function, e^{-x}. It therefore exhibits a rise and a fall, as shown below:
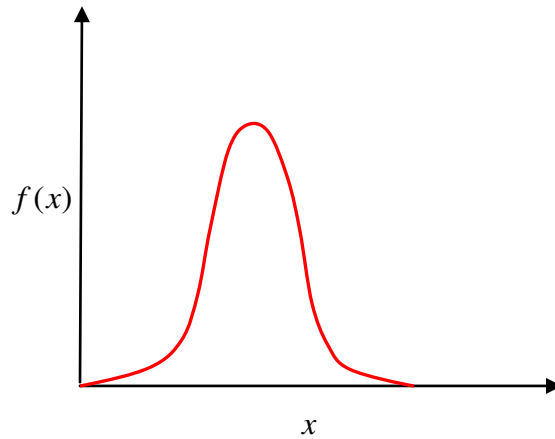
For large values of n, the function $f(x)$ is quite sharply peaked, so its integral will be dominated by values of x near the maximum, since everywhere else it is practically 0. It is expected to be well approximated, therefore, by a second-order Taylor's expansion around this maximum. This approximation to $f(x)$ will allow the integral in Eq. (6) to be evaluated analytically.

To find the maximum in $f(x)$, we differentiate it with respect to x and set the result to 0:

$$\frac{df}{dx} = 0 = nx^{n-1}e^{-x} - x^n e^{-x} = x^{n-1}e^{-x}(n-x) \tag{7a}$$

$$\therefore x_{\text{max}} = n \tag{7b}$$

The Taylor's expansion of $f(x)$ around x_{max} is now given by

$$f(x) \approx f(x_{\text{max}}) + (x - x_{\text{max}})\frac{df}{dx}\bigg|_{x=x_{\text{max}}} + \frac{1}{2}(x - x_{\text{max}})^2 \frac{d^2 f}{dx^2}\bigg|_{x=x_{\text{max}}} + \cdots \tag{8a}$$

$$= f(x_{\text{max}}) + \frac{1}{2}(x - x_{\text{max}})^2 \frac{d^2 f}{dx^2}\bigg|_{x=x_{\text{max}}} + \cdots \tag{8b}$$

(The first derivative in Eq. (8a) vanishes by virtue of the maximization condition (7a)). The second derivative is

$$\frac{d^2 f(x)}{dx^2} = (n-1)x^{n-2}e^{-x}(n-x) - x^{n-1}e^{-x}(n-x) - x^{n-1}e^{-x}$$

$$\therefore \frac{d^2 f(x)}{dx^2}\bigg|_{x=x_{\text{max}}=n} = -n^{n-1}e^{-n} \tag{9}$$

Substituting Eq. (9) into Eq. (8b), along with $f(x_{\text{max}}) = f(n) = n^n e^{-n}$, we end up with

$$f(x) \approx n^n e^{-n} - \frac{1}{2}(x-n)^2 n^{n-1}e^{-n}$$

$$= n^n e^{-n}\left[1 - \frac{1}{2n}(x-n)^2\right]$$

$$\approx n^n e^{-n} \exp\left[-\frac{1}{2n}(x-n)^2\right] \tag{10}$$

The step from the second to the third line of Eq. (9) makes use of the general result $1 - y \approx e^{-y}$ for $y \ll 1$. It is introduced to produce a functional form for $f(x)$ that is easy to integrate. So substituting Eq. (10) into the RHS of Eq. (6), we get

$$n! = \int_0^\infty dx\, n^n\, e^{-n}\, \exp\left[-\frac{1}{2n}(x-n)^2\right]$$

$$= n^n\, e^{-n} \int_0^\infty dx\, \exp\left[-\frac{1}{2n}(x-n)^2\right] \tag{11}$$

The introduction of the following change of variable is helpful at this point: $z = x - n$. It transforms Eq. (11) to

$$n! = n^n\, e^{-n} \int_{-n}^\infty dz\, e^{-z^2/2n} \tag{12}$$

Because n is large, very little error is caused by extending the lower limit in this integral to $-\infty$. Then, making use of the identity $\int_{-\infty}^\infty dy\, e^{-Ay^2} = \sqrt{\pi/A}$, Eq. (12) finally reduces to

$$n! = n^n\, e^{-n}\, \sqrt{2\pi n} \tag{13}$$

and the logarithm of this expression becomes

$$\ln n! = n \ln n - n + \frac{1}{2}\ln(2\pi n) \tag{14}$$

Retaining just the largest terms in this expression, we arrive at Stirling's approximation

$$\ln n! \approx n \ln n - n \tag{15}$$

• Back to the derivation of the fundamental equation

With Stirling's approximation in hand, we can simplify Eq. (5) to

$$\ln \Omega = (U/\hbar\omega + 3N)\ln(U/\hbar\omega + 3N) - (U/\hbar\omega + 3N) - (U/\hbar\omega)\ln(U/\hbar\omega)$$

$$+ (U/\hbar\omega) - 3N \ln 3N + 3N \tag{16}$$

After cancellation of terms, Eq. (16) becomes

$$\ln \Omega = (U/\hbar\omega + 3N)\ln(U/\hbar\omega + 3N) - (U/\hbar\omega)\ln(U/\hbar\omega) - 3N \ln 3N \tag{17}$$

Pulling out a factor of $3N$ from the first term in this expression, we get

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$$\ln \Omega = 3N \left(1 + \frac{U}{3N\hbar\omega} \right) \ln \left[3N \left(1 + \frac{U}{3N\hbar\omega} \right) \right] - \frac{U}{\hbar\omega} \ln \frac{U}{\hbar\omega} - 3N \ln 3N \qquad (18)$$

which can be re-arranged to

$$\ln \Omega = 3N \left[\left(1 + \frac{U}{3N\hbar\omega} \right) \ln 3N + \left(1 + \frac{U}{3N\hbar\omega} \right) \ln \left(1 + \frac{U}{3N\hbar\omega} \right) - \frac{U}{3N\hbar\omega} \ln \frac{U}{\hbar\omega} - \ln 3N \right] \quad (19)$$

and after cancellation of the terms in $\ln 3N$, followed by further rearrangements, we're left with

$$\ln \Omega = 3N \left[\frac{U}{3N\hbar\omega} \ln \frac{3N\hbar\omega}{U} + \left(1 + \frac{U}{3N\hbar\omega} \right) \ln \left(1 + \frac{U}{3N\hbar\omega} \right) \right] \qquad (20)$$

This is almost the final result, but it can be made more compact by suitably redefining parameters; it helps, in particular, to do the following: (i) introduce factors of Avogadro's number $\mathfrak{N}_A$ to convert N, the number of atoms, into n, the number of moles, through the relation $n = N / \mathfrak{N}_A$, (ii) multiply Eq. (17) by Boltzmann's constant k_B, (iii) introduce the gas constant R through the relation $R = k_B \mathfrak{N}_A$, (iv) replace $3\mathfrak{N}_A \hbar\omega$ by u_0, and (iv) express S and U in molar form through the definitions $u = U / n$ and $s = S / n$. These steps finally lead to

$$s = 3R \left[\frac{u}{u_0} \ln \frac{u_0}{u} + \left(1 + \frac{u}{u_0} \right) \ln \left(1 + \frac{u}{u_0} \right) \right] \qquad (21)$$

which can also be re-written as

$$s = 3R \left[\frac{u}{u_0} \ln \frac{u_0}{u} \left(1 + \frac{u}{u_0} \right) + \ln \left(1 + \frac{u}{u_0} \right) \right] \qquad (22)$$

which is the same as

$$s = 3R \left[\frac{u}{u_0} \ln \left(1 + \frac{u_0}{u} \right) + \ln \left(1 + \frac{u}{u_0} \right) \right] \qquad (23)$$

and this then is the final form of the fundamental equation of an Einstein solid.

• Thermodynamic predictions

Several properties of the solid can be calculated from Eq. (23).

1. *Temperature and energy*

For instance, from the relation

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N = \left(\frac{\partial s}{\partial u}\right) \tag{24}$$

we find, after differentiating (23) with respect to $u,$ that

$$\frac{1}{T} = 3R\left[\frac{1}{u_0}\ln\left(1+\frac{u_0}{u}\right)+\frac{u}{u_0}\frac{1}{(1+u_0/u)}\left(-\frac{u_0}{u^2}\right)+\frac{1}{(1+u_0/u)}\frac{1}{u_0}\right] \tag{25}$$

which after cancellation of terms becomes

$$\frac{1}{T} = \frac{3R}{u_0}\ln\left(1+\frac{u_0}{u}\right) \tag{26}$$

This can be rearranged first to

$$1+\frac{u_0}{u} = e^{u_0/3RT} \tag{27}$$

and then to

$$u = \frac{u_0}{e^{u_0/3RT}-1} \tag{28}$$

2. *The heat capacity*

For a substance at constant V and n (n being the number of moles) the differential form of the energy dU is simply

$$dU = TdS$$

If this relation is divided by n and dT, we arrive at

$$\left(\frac{\partial u}{\partial T}\right)_{V,n} = T\left(\frac{\partial s}{\partial T}\right)_{V,n} \tag{29}$$

where, as before, $u = U/n$ and $s = S/n$. But the RHS of this equation is just the definition of the molar heat capacity at constant volume c_V, so by differentiating Eq. (28) with respect to T at constant V and n, we can calculate c_V (of course, there's no volume dependence in Eq. (28), but that doesn't affect the process of taking the derivative.) Calculating c_V in this way, we find that

$$\frac{du}{dT} = c_V = -\frac{u_0}{\left(e^{u_0/3RT} - 1\right)^2}\left(-\frac{u_0}{3RT^2}\right)e^{u_0/3RT}$$

$$= \frac{u_0^2}{3RT^2}\frac{e^{u_0/3RT}}{\left(e^{u_0/3RT} - 1\right)^2} \tag{30}$$

Limiting behavior of the heat capacity

As written, Eq. (30) is somewhat opaque, but it simplifies when the temperature is either very high or very low. In the limit of high temperatures, we can take $u_0/3RT$ to be very small; the exponentials in Eq. (30) can then be approximated by the leading terms in their Taylor expansion. For the exponential in the numerator of Eq. (30), this means

$$e^{u_0/3RT} \approx 1 + \cdots \tag{31}$$

while for the exponential in the denominator it means

$$e^{u_0/3RT} - 1 \approx 1 + \frac{u_0}{3RT} + \cdots - 1$$

$$= \frac{u_0}{3RT} + \cdots \tag{32}$$

The substitution of these results into Eq. (30) leads to

$$c_V \xrightarrow{T \gg 1} 3R \tag{33}$$

In the limit of low temperatures, we can take $u_0/3RT$ to be very large; the exponentials in Eq. (30) then become very large too, so the factor of 1 in the denominator can be discarded. After this step, what remains is

$$c_V = \frac{u_0^2}{3RT^2}e^{-u_0/3RT}$$

$$\approx 0 \tag{34}$$

Given these limiting behaviors of c_v (cf. Eqs. (33) and (34)), its overall temperature dependence looks like this:
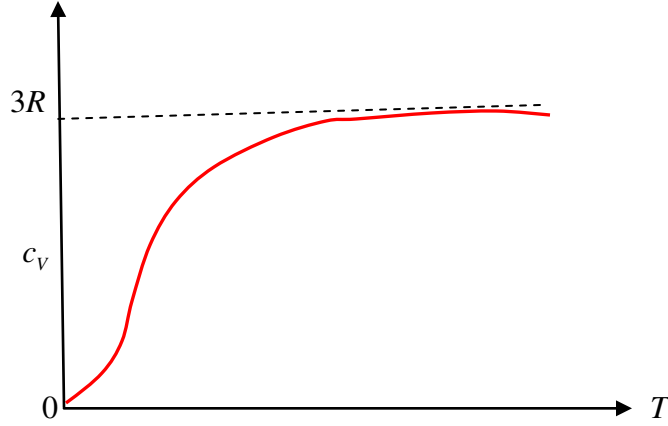
• <u>Comparing theory and experiment</u>

The high temperature behavior of the constant volume molar heat capacity of the Einstein solid actually reproduces experimental data on crystalline solids, which all asymptote to the value of $3R$ predicted by the present calculations.

This asymptotic behavior is known as <u>Dulong and Petit's Law</u>, and is simply explained by the <u>equipartition theorem</u>, which states that each quadratic degree of freedom possessed by the atoms of a system contributes $\frac{1}{2}k_BT$ to the system's overall energy. A degree of freedom is one of the 3 Cartesian coordinates x, y or z, or one of the 3 velocity components v_x, v_y or v_z along these directions. An atom in a solid has 3 translational degrees of freedom and 3 vibrational degrees of freedom. Translational energy is of the form $\frac{1}{2}mv_x^2$ (along a given Cartesian coordinate), so from the 3 translational degrees of freedom, each atom contributes $\frac{3}{2}k_BT$ to the total energy. Vibrational energy is of the form $\frac{1}{2}kx^2$ (along a given Cartesian coordinate), so from the 3 vibrational degrees of freedom, each atom contributes another $\frac{3}{2}k_BT$ to the total energy. Per mole then, the total energy is $3RT$. The derivative of this quantity with respect to T, which is the heat capacity, is $3R$, and this is the Dulong and Petit Law.

At low temperatures, the dependence of c_V on T as predicted by the Einstein model is actually wrong, as it goes to 0 too quicky. The actual low temperature behavior of c_V is better described by $c_V \sim T^3$.

The mechanical properties of the Einstein solid are also wrong. The fact that the entropy of the solid is independent of the volume means that its pressure – as given by $P = T(\partial s / \partial v)_u$ – is identically 0. The solid therefore cannot oppose forces applied to it – it is infinitely compressible!

But given the simplicity of the model, it is quite remarkable that it nevertheless does a very good job of capturing the broad trends in at least some of the observed thermodynamic properties of real solids. This suggests that the statistical mechanical approach we have developed of counting a system's microstates and then appealing to the Boltzmann equation to make the link to thermodynamics is a reasonable method of predicting or rationalizing the behavior of matter in the bulk. We'll see more examples of its general utility in the lectures to come.